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SUPERCONDUCTIVITY IN NONSTOICHIOMETRIC COMPOUNDS, LAYERS, AND C--ETC(U)

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SUPERCONDUCTIVITY IN NONSTOICHIOMETRIC COMPOUNDS,  
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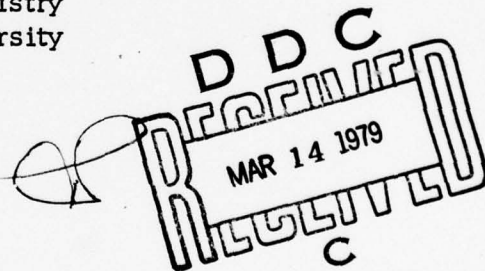
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## ABSTRACT

The objective of this research was to study the effect of chemical composition on superconductivity in chemical compounds. Four kinds of compounds were investigated: tunnel-structure tungsten bronzes, covalent-frame hexaborides, layered-structure transition metal dichalcogenides, and Chevrel-type molybdenum ternaries. In the tungsten bronzes, it was found that changing electron density was less important than enhancing electron-phonon coupling, as by approach to a crystallographic structure change boundary. In the metal hexaborides, it was shown that lattice expansion was less effective than decreasing conduction electron density in depressing the superconducting critical temperature, but even more effective was presence of magnetic ions in the metal sublattice. This was found to be the most likely reason for the very low critical temperature of lanthanum hexaboride. In the layered dichalcogenides, insertion of magnetic ions between the layers was found to be less effective in depressing critical temperature than either substitution of magnetic ions within the layers or departure from stoichiometry. The latter was found to lead to a change in polytype which could be correlated with the onset temperature of a charge density wave. In the Chevrel-type compounds, a new correlation was found between superconducting critical temperature,  $c/a$  lattice parameter ratio, and deviation from stoichiometry.

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This report is divided into five sections. The first gives a general view of the scope and rationale of the investigation. The second details the specific findings on the systems studied. The third summarizes problems that remain unsolved and deserve further investigation. The fourth describes the personnel who participated in the work. The fifth and final part lists the publications that have come out of the investigation together with those which are in preparation. The support of the AFOSR is gratefully acknowledged.

## I. SCOPE and RATIONALE

This work started as the aftermath of a discovery by Wanlass and Slenko [J. Solid State Chem. 12 362(1975)] that the superconducting critical temperature in rubidium tungsten bronze ( $\text{Rb}_x\text{WO}_3$ ) did not follow the expected increase with  $x$  as conduction electron density increased but showed a totally unexpected pair of peaks at  $x = 0.20$  and at  $x = 0.30$ . The tungsten bronzes  $\text{M}_x\text{WO}_3$  ( $0 < x < 1$ ) are a series of nonstoichiometric compounds where donor metal atoms  $\text{M}$  act as interstitial dopants of a host  $\text{WO}_3$  structure. The host stoichiometric structure is a wide-gap semiconductor (2.4 eV) which undergoes a metal-nonmetal transition when  $x$  exceeds 0.2. In addition there is a successive increase in the symmetry of the structure as the relative content of  $\text{M}$  in  $\text{WO}_3$  increases. In the limit, the structure becomes cubic but, in spite of the very high density of states at the Fermi level, none of the cubic bronzes is a superconductor, apparently because the electron-phonon coupling is too weak. The hexagonal and tetragonal bronzes, however, are Type II superconductors. Specifically  $\text{Rb}_x\text{WO}_3$ , which is hexagonal in the range



$0.17 < x < 0.33$ , shows critical temperatures as high as  $4.4^{\circ}\text{K}$ . The fact that these could be raised to  $7.7^{\circ}\text{K}$  by acid etching led to the original investigation of  $T_c$  as a function of rubidium content. As described in part II, the original idea that the enhanced  $T_c$  was due to replacement of H for Rb turned out to be false and the main effect is to move the composition to the phase boundary of the hexagonal range.

Because ammonium ion is chemically very similar to rubidium ion, a series of ammonium tungsten bronzes were also synthesized and examined for superconductivity in this investigation. Unlike the alkali tungsten bronzes, which are rather inert chemically, the ammonium bronzes are sensitive to moisture and oxygen, so it was difficult to establish the concentration dependence of superconductivity. Two important findings were that the properties of the materials depended on the path by which the materials were made and, most surprising, the critical temperature did not correlate well with the content of ammonia but with the reducing power of the materials. Subsequent study showed that the materials contained two kinds of ammonia, part as  $\text{NH}_3$  and part as  $\text{NH}_4^+$ . It appears that these occur as pairs, perhaps as the species diammonium,  $\text{N}_2\text{H}_7^+$ , stuck in the hexagonal channels of the structure. Because of the difficulty of making these materials superconducting in a reproducible way and because the  $T_c$  values were limited (rarely above  $3^{\circ}\text{K}$ ), this line of investigation was abandoned.

It became early evident that superconductivity in the tungsten bronzes would be limited because, as concentrations were manipulated near the hexagonal phase boundary, the materials quickly became unstable to a hexagonal-monoclinic transition. None of the monoclinic materials was superconducting. In casting

about for a more rigid structure, which would also be capable of chemical manipulation of a metal-nonmetal transition, we turned to the metal hexaborides. These are very rigid cubic structures in which metal atoms occupy the body-centered position of a cube, and corner-connected octahedra of boron atoms occupy the cube corner positions. The  $B_6$  framework in this simple cubic geometry has two hole states per unit cell. Insertion of an alkali atom, e.g. Na, in the M position of  $MB_6$  fills one of the hole states, so  $NaB_6$  is a metal. Insertion of an alkaline earth atom, e.g. Ca, fills both of the hole states, so  $CaB_6$  is a nonmetal. What happens when M of  $MB_6$  is trivalent? The third electron goes to the next available band, partially fills it, and makes  $MB_6$  metallic. Consequently, by using a mixture of divalent and trivalent M, it should be possible to manipulate the conduction electron density. Furthermore, by judicious choice of M, magnetic ions can be introduced and the ratio of conduction electrons to magnetic ion concentration varied. Some work of this kind is described in the publication list at the end of this report.

One of the mysterious aspects of the hexaborides is that lanthanum hexaboride,  $LaB_6$ , which presumably contains the diamagnetic  $La^{3+}$  ion, has such a low superconducting critical temperature ( $0.1^\circ K$ ). The band structure and phonon spectrum of  $LaB_6$  have been worked out so calculation of the electron-phonon coupling constant should be possible. The results suggest that  $T_c$  of  $LaB_6$  should be of the order of  $30^\circ K$ . In an attempt to discover why the observed superconductivity turns out to be so much lower, we first synthesized ultra-pure  $LaB_6$  to assure ourselves it was not trace magnetic impurity that was quenching the superconductivity. Then we investigated the related compound  $YB_6$ , which shows the perfectly respectable superconducting critical temperature of  $6.0^\circ K$ ,

and particularly the influences of lattice expansion, conduction electron density, and presence of magnetic moments. As indicated in part II, it was concluded that the most probable reason for lack of superconductivity in  $\text{LaB}_6$  is a small amount of intrinsic magnetic moment, possibly arising from trace amounts of  $\text{La}^{+2}$  in the pure stoichiometric material.

Although at one time the layered compounds offered great promise as vehicles for study of dimensionality effects on superconductivity, subsequent studies failed to produce evidence of the hoped-for decoupling. Still, the unusual electric and magnetic properties of these materials can be used to advantage to study chemical control of superconductivity. The basic feature of a layered dichalcogenide is a two dimensional sandwich in which a sheet of metal atoms M is interleaved between two adjacent layers of hexagonal-packed chalcogen atoms X (where X = S, Se, or Te). The stoichiometry is  $\text{MX}_2$  and the local geometry of X about M is either trigonal prismatic or distorted octahedral. Nonbonded stacking of the sandwiches on top of each other gives rise to a van der Waals gap between layers and leads to various polytypes, which are different structures with different relative arrangements of trigonal prisms and octahedra along the stacking axis. If M is a subgroup IV element (Ti, Zr, Hf, Sn) or a subgroup VI element (Cr, Mo, W),  $\text{MX}_2$  is generally nonmetallic; if M is a subgroup V element (V, Nb, Ta),  $\text{MX}_2$  is metallic.  $\text{NbX}_2$  and  $\text{TaX}_2$  are superconducting but  $\text{VX}_2$ , although it should be, is not. In this investigation the superconductivity of  $\text{MX}_2$  was examined as a function of several chemical variables, most notably departure from stoichiometry and partial replacement of one element by another.

When  $\text{MX}_2$  goes off stoichiometry as  $\text{M}_{1+x}\text{X}_2$ , the departure from



stoichiometry can be brought about by an excess of the metal M or by a deficit of the nonmetal X. Both types of defects occur, but as yet there is no clear way to establish quantitatively the exact concentration of each. For the layered dichalcogenides it is generally believed that the predominant defect causing nonstoichiometry is excess metal M located in interstitial positions in the van der Waals gap between sandwiches. How does it affect superconductivity? As noted below for our study of niobium dichalcogenides, excess niobium per se has relatively little effect in depressing  $T_c$ . However, in the specific case of niobium disulfide, excess niobium induces a change in polytype from 2H (the hexagonal 2-layer stack) to 3R (a rhombohedral 3-layer stack) and this produces a dramatic quenching of superconductivity. This is not expected. Both 2H and 3R polytypes of  $\text{NbS}_2$  have trigonal prismatic arrangement of sulfur atoms around the niobium and the excess niobium appears to be nonmagnetic, so the quenching of superconductivity in  $3\text{R-Nb}_{1+x}\text{S}_2$  must arise from some more subtle kind of coupling between the layers.

Because the electrical coupling between layers leads to charge density waves (CDW) and periodic lattice distortions (PLD) and because there seems to be an empirical anti-correlation between CDW and superconductivity, part of this investigation was devoted to a study of chemical effects (nonstoichiometry and atom substitution) on CDW. In particular, the compound  $\text{VSe}_2$  was studied in some detail.

$\text{VSe}_2$  is a metal with a CDW onset at about  $110^\circ\text{K}$  and no superconductivity even down to  $0.05^\circ\text{K}$ . Believing that it was slight excess vanadium as  $\text{V}_{1+x}\text{Se}_2$  which was quenching the superconductivity, we investigated both the super-



conductivity and the CDW onset as a function of departure from stoichiometry and replacement doping of niobium for vanadium. Unlike the situation in all other systems investigated, where impurities depress the onset of CDW, here we find that the CDW is enhanced!

One of the problems involved in partially replacing a metal atom M of  $MX_2$  by some other metal M' is to know where the substituting metal goes--in the layer or in the gap. This is still an unresolved question but we have done in this investigation three studies that highlight the complexities involved. One of these was a study of vanadium-substituted niobium diselenide. As x increases for  $V_xNb_{1-x}Se_2$ , the  $T_C$  drops very rapidly from 7.2°K to 4°K for the first 1%, then flattens out and remains at about 3°K for about 20%. As described below, the first 1% of V goes substitutional for Nb in trigonal prismatic layers but then there is an abrupt appearance of interleaving octahedral layers. Apparently, vanadium likes octahedral coordination so strongly that it persuades the niobium in half the layers to become octahedral also. Only the trigonal prismatic layers remain superconducting. The octahedral layers are metallic but do not superconduct; they have a characteristic charge density wave distortion which, again contrary to expectation, increases as the vanadium content is increased.

A second substitutional system we studied was  $V_xTi_{1-x}S_2$ . The reason for studying this material was the anomaly of  $TiS_2$ . As a subgroup IV element, Ti is expected to give a nonmetallic  $TiS_2$ , the four valence electrons of the titanium just being able to fill the holes in the sulfur band. However, the observed fact is that  $TiS_2$ , even when stoichiometric, is a metal. One possible model for the metallic behavior is that part of the titanium may be anti-structural,

that is, occurring not in the normal octahedral sites of the sandwich but in some of the normally empty octahedral sites between sandwiches. In an attempt to define the characteristics of the titanium states in this material, a study was carried out of the vanadium-substituted series  $V_xTi_{1-x}S_2$  ( $0 \leq x \leq 0.5$ ). As noted below, there is observed a totally unexpected shift from metallic to semiconductive behavior, with magnetic effects playing an essential role, especially at low temperatures, in causing anomalous resistivity behavior.

Revelli [Ph.D. Thesis, Stanford University, 1973] had discovered some time ago that the other members of subgroup IV, the zirconium and hafnium disulfides and diselenides, could be made superconducting by intercalating alkali metals in the van der Waals gap. In a rigid band model, this can be understood as resulting from population of the layer's conduction band by donor action of the intercalate. However, there is a gradation of  $T_c$  inversely with mass ( $1.88^\circ K$  for Li,  $1.4^\circ K$  for Na, and  $0.98^\circ K$  for K in  $HfS_2$ ) which suggests that the superconductivity is associated with the alkali atoms rather than with the  $HfS_2$ . For this reason we undertook an investigation of the  $HfS_{2-x}$  ( $0 < x < 1$ ) system, the  $HfTe_{2-x}$  ( $0 < x < 0.6$ ) system, and the mixed system  $HfSe_{2-x}Te_x$  ( $0 < x < 2$ ). The latter showed an interesting metal-nonmetal transition at  $x = 0.1$  but no superconducting materials were found in the study.

Closely related to the subgroup IV dichalcogenides are the subgroup VI materials, typified by  $MoS_2$ . This is a 1.5-eV gap semiconductor, which on intercalation with alkali metal has been reported to become superconducting with transition temperatures as high as  $4.5^\circ K$  [Somoano and Rembaum, J. Chem. Phys. 58 697(1973)]. At the present time, there is doubt that the superconducting phase is indeed as suggested  $MoS_2$  to which alkali metal has

simply contributed conduction electron density; it appears rather that chemical reduction has occurred with formation of a new, as yet unidentified, phase. Because of the group resemblance of molybdenum to tungsten, the element below it, we have investigated in this program the tungsten dichalcogenides, particularly the mixed systems in which anion-for-anion substitution has occurred. Although, as noted below, interesting crystallographic changes are observed, none of the materials, including alkali-intercalated specimens, showed any sign of superconductivity. An abortive effort to prepare  $W_3S_4$  and  $W_3Se_4$ , analogous to the superconducting  $Mo_3S_4$  and  $Mo_3Se_4$ , ended up in failure.

Layered compounds, doped or off stoichiometry, seem to be limited to superconducting critical temperatures below  $7^\circ K$ . Even the most careful syntheses, using ultrapure materials and precise stoichiometry, cannot get away from this apparent ceiling. As the electron density has been varied over several orders of magnitude with but little positive effect, it appears that some limitation, perhaps too weak a metal-metal bonding, is at the root of the low  $T_c$ . Apparently more promising as superconducting compounds are the Chevrel compounds, typified by  $M_x Mo_6 S_8$  ( $M = Pb, Sn, Cu, \text{etc.}$ ). These exhibit a large number of unusual properties--high  $T_c$  (up to  $16^\circ K$ ), highest critical fields yet observed, enormous pressure dependence of  $T_c$ , and, most surprising of all, coexistence of magnetic ions and superconductivity. The final part of the investigation concerned itself with a study of Chevrel compounds.

The main problem with Chevrel compounds is that they are invariably contaminated with other phases. For this reason, it has been difficult to investigate the relationship between stoichiometry and superconductivity, although these ternary chalcogenides should provide a unique opportunity for

studying the connection between composition and electronic properties. Attempts to grow single crystals of  $\text{PbMo}_6\text{S}_8$  and  $\text{SnMo}_6\text{S}_8$  have so far been unsuccessful, but analysis of powder crystallographic data on  $\text{Mo}_6\text{X}_8$  compounds and their derivatives  $\text{M}_x\text{Mo}_6\text{X}_8$ , has disclosed that, when the ternary element (e.g. Pb in  $\text{Pb Mo}_6\text{S}_8$ ) in a series of Chevrel phases has the same formal valence, the superconducting transition temperature is found to be a very sensitive linear function of the  $c/a$  ratio. Since the  $c/a$  ratio is essentially a normalized  $c$  axis, it is believed that the observed linearity arises from the low frequency longitudinal phonon modes which run along the  $c$  axis. Raman spectroscopy studies of the shifting soft modes as a function of  $c/a$  are still in progress at this writing.

## II. SPECIFIC FINDINGS

In this section, condensed abstracts are given for detailed findings on the above problems. They are arranged by topics (bronzes, borides, layers, ternaries) and by name of researcher who made principal contributions.

### (A) BRONZES

(1) David R. Wanlass, "Concentration Dependence of Superconductivity in Rubidium Tungsten Bronzes", published J. Sol. State Chem. 12 362(1975)

Rubidium tungsten bronzes of composition  $\text{Rb}_x\text{WO}_3$  ( $0.20 < x < 0.30$ ) have been prepared in well-defined crystalline form and examined for superconductivity by flux-exclusion techniques. An unusual double maximum with peak values in the critical temperature of  $4.35^\circ\text{K}$  at  $x = 0.20$  and  $2.90^\circ\text{K}$  at  $x = 0.30$  is observed. One possible explanation is enhanced electron-phonon



coupling associated with ordering of rubidium occupancy in the hexagonal tunnels. The effect of acid etching was also examined; it was concluded that an observed increase in critical temperature is not due to hydrogen replacement for rubidium as was postulated. Critical magnetic field studies indicate type II behavior consistent with the Abrikosov-Ginzburg equation.

(2) Jack F. Thomas "Low Temperature Magnetic Susceptibility of Uranium and Rare Earth Tungsten Oxide Bronzes", published in J. Chem. Phys. 61 3920(1974).

Magnetic susceptibilities of uranium tungsten bronzes,  $U_xWO_3$ , and their thorium-diluted counterparts,  $U_xTh_{0.10-x}WO_3$ , have been measured by the Faraday method over the range 1.6-300°K. The sharp, dilution-independent antiferromagnetic behavior previously reported by Ostertag was not confirmed. Weiss constants observed showed a weak decline with dilution. Susceptibilities of light rare earth bronzes (RE=Pr, Nd) deviated at low temperature from Curie-Weiss behavior, probably because of changes in population of intra-atomic levels. For the heavy rare earth bronzes (RE=Gd, Tb, Dy, Ho, Er) very small Weiss constants were observed. Near independence of the Weiss constants of conduction electron density and rare earth magnetic content suggests that the apparent Curie-Weiss behavior is mainly a manifestation of crystal field interactions, not an indication of magnetic exchange effects.

(3) Benoy K. Chakraverty, "Low-temperature Specific Heat and Magnetic Susceptibility of Nonmetallic Vanadium Bronzes", published in Phys. Rev. 17B 3781(1978)

A linear  $\gamma T$  term is observed in the low-temperature specific heat behavior of the nonmetallic vanadium oxide bronzes of sodium and copper.

The low-temperature magnetic susceptibility is equally anomalous and points to a singlet or diamagnetic ground state. It is postulated that the  $V^{4+}$  centers in these bronzes form near-neighbor pairs or bipolarons through deformation-induced attraction. The tunneling of these bipolarons between pairs of sites gives rise to the linear term of the specific heat. The progressive breaking up with temperature of the singlet bipolarons provides a natural explanation of both the magnetic susceptibility as well as of the electrical conductivity. It is believed that the localized Cooper pairs invoked in these bronzes may be the precursor of superconductivity.

(4) Johannes Kaas Petersen, "Concentration Dependence of Superconductivity in Ammonium Tungsten Bronzes."

Ammonium tungsten bronzes,  $(NH_4)_xWO_3$  ( $0 < x < 0.45$ ), have been prepared by thermal decomposition of ammonium paratungstate under a variety of conditions (temperature, ambient atmosphere). Electric and magnetic properties are observed to depend on the path by which the material is made. Studies by measurement of chemical reducing power indicated that the ratio of  $NH_4^+$  to  $e^-$  is not unity as expected from other bronzes, but can be increased by carrying out the decomposition at higher pressures of ammonia or lower pressures of hydrogen. The most consistently obtained ratio was 2:1 suggesting formation of a new species, diammonium ion,  $N_2H_7^+$ , composed of a neutral ammonia molecule hydrogen-bonded to an ammonium ion and stabilized by trapping in the hexagonal tunnels of the structure. Superconducting critical temperatures were in the range 1.5-3.5°K and correlated better with reducing power than with ammonia content.

(5) Andrejs Lusis, "Search for Superconductivity in Photochromic Tungsten Trioxide."

Single crystals of  $\text{WO}_3$  were colored by electrochemical reduction in acidic solution. The materials ranged from blue to bronze and are believed to correspond to hydrogen tungsten bronze,  $\text{H}_x\text{WO}_3$ . Search for the hydrogen by pulsed NMR studies indicated two relaxation times, one of which is rather short. ESR studies gave no signals at room temperature but cooling to liquid helium generated a resonance which then persisted to room temperature. It could be destroyed by annealing. A large conductivity anomaly was observed in a Meissner-type experiment at  $\sim 28^\circ\text{K}$ . It apparently is connected with a magnetic transition. Properties of the crystals were time-dependent. Only freshly prepared materials showed the effects described.

(B) BORIDES

(1) Rudolf Sobczak, "Superconductivity in the Hexaborides", in press J. Less-Common Metals.

Powder samples of the mixed hexaborides  $(\text{Y},\text{La})\text{B}_6$  have been prepared by borothermal reduction. Superconducting transition temperatures, as measured by static Faraday susceptibility and by Meissner flux expulsion, were observed to range from  $6.0 \pm 0.1^\circ\text{K}$  for  $\text{YB}_6$  to  $1.6 \pm 0.1^\circ\text{K}$  for  $\text{Y}_{0.5}\text{La}_{0.5}\text{B}_6$ . The influence of impurities Yb, Ce, Nd, Fe, Ba, and Ca has been systematically explored. Even the highest amount of iron (0.3%) that could replace yttrium was not able to destroy the superconductivity of  $(\text{Y}, \text{Fe})\text{B}_6$  ( $T_c = 3.3^\circ\text{K}$ ). On the other hand, very small amounts of ytterbium (0.005%) lower the  $T_c$  about the same amount as does a much larger amount of iron. A smaller amount

of cerium than iron lowered the  $T_C$  value more. Apparently localized f electrons are more effective in lowering  $T_C$  than are localized d electrons. Measurements of the susceptibility suggest that the very low critical temperature of  $\text{LaB}_6$  ( $0.1^\circ\text{K}$ ) is due to a small magnetic moment coming from the lanthanum itself. The change of lattice parameter is of only minor influence on the superconductivity.

(2) Jerry L. Krause, "Antiferromagnetic Coupling in Ytterbium-Diluted Dysprosium Hexaborides", published in J. Chem. Phys. 64 4265(1976).

A series of dysprosium hexaborides in which dysprosium was progressively replaced by ytterbium have been prepared by high temperature reaction between elemental boron and rare earth oxide. Magnetic susceptibility measurements have been performed by the Faraday method over the range  $1.6\text{--}300^\circ\text{K}$ . In the interval  $63\text{--}300^\circ\text{K}$ , the susceptibilities follow Curie-Weiss laws with an effective moment per dysprosium of  $10.6 \pm 0.3$  Bohr magnetons. The Weiss constants are relatively small, having values of  $-21.5$ ,  $-18.5$ ,  $-14.0$ ,  $-11.5$ , and  $-7.5^\circ\text{K}$  in  $\text{Dy}_x\text{Yb}_{1-x}\text{B}_6$  at  $x = 1, 0.8, 0.6, 0.4$ , and  $0.2$ , respectively. Below  $60^\circ\text{K}$ , the materials show antiferromagnetism; Néel temperatures were observed to decrease in the sequence  $21, 16, 8$ , and  $2^\circ\text{K}$  for the first four of the above compositions. Interpretation of results via statistical analysis of two, three, and greater-than-three clusters indicates that when isolated magnetic ions are corrected for, the residual magnetism corresponds to a constant exchange energy  $J$ , independent of conduction electron concentration. There is no direct evidence that indirect exchange, via conduction electrons plays a role in the magnetic interaction.

#### (C) LAYERS

(1) Bernard Mentzen, "Preparation and X-Ray Study of Mixed-Anion



Dichalcogenides", published in Inorg. Chem. 15 2198(1976).

Mixed-anion systems of the tungsten dichalcogenides have been prepared by direct synthesis from the elements. X-ray investigations have been carried out as a function of composition. In the  $WS_{2-x}Se_x$  system, there is a continuous series of solid solutions, all having the 2H structure (space group  $P6_3/mmc$ ). The unit-cell parameters increase monotonically as  $x$  increases, but there is a maximum in the  $c/a$  ratio at  $x = 1.3$ . In the  $WSe_{2-x}Te_x$  system, monophasic regions occur for  $0 < x < 0.62$ , where the structure is 2H, and  $1.48 \leq x \leq 2.00$ , where the structure is that of  $WTe_2$  (space group  $Pnm2_1$ ). In the  $WS_{2-x}Te_x$  system, corresponding monophasic regions occur for  $0 < x < 0.3$  and  $1.8 \leq x \leq 2.0$ .

In going from  $WS_2$  and  $WSe_2$  to  $WTe_2$ , there is not only a change from trigonal-prismatic to approximately octahedral coordination but there is also a decided change in metallic character. Whereas  $WS_2$  and  $WSe_2$  are semiconductors with band gaps of the order of 0.1 eV,  $WTe_2$  is a semimetal. Starting with a covalent model for  $WTe_2$  and assuming an octahedral environment for the tungsten (the actual distortion is relatively slight), the bonding in  $WTe_2$  can be described as  $\sigma$  covalence between  $d_{\gamma}^2 sp^3$  hybrids of the W and  $sp^3$  hybrids of the tellurium, overlaid by a conduction band composed of W  $5d_e$  orbitals (with perhaps some Te 5d character). The latter would be unoccupied except for transfer of one-third of an electron from each of the surrounding six Te atoms. The presence of three orbitals for a total of two electrons would be consistent with the metallic character.

The effect of substituting selenium or sulfur for tellurium would be

to pull electron density away from the tungsten in the tungsten-chalcogen bond, weaken the incipient W-W bond, and break up any possibility of a W 5d overlap band. Carrier mobility data could clarify the mechanism by which band breakup occurs. It appears that carrier mobility should go from a  $T^{-3/2}$  dependence characteristic of acoustic phonon scattering in stoichiometric  $WTe_2$  to an activated-hopping type in the anion-doped systems. Attempts were made in this research to grow large single crystals of the mixed-anion compounds by vapor-phase transport for electrical studies, but ion-probe analysis indicated that stoichiometry was not homogeneous along such a crystal.

(2) Michel Bayard, Bernard Mentzen, "Synthesis and Structural Aspects of the Vanadium-Substituted Niobium Diselenides", published in Inorg. Chem. **15** 1763(1976).

Solid solutions of formula  $Nb_{1-x}V_xSe_2$  ( $0 < x < 1$ ) have been prepared by direct synthesis from the elements under minimum-gradient conditions. Single crystals of  $NbSe_2$  and  $VSe_2$  have been made by chemical transport using iodine as transporting agent. X-ray studies by single-crystal and Debye-Scherrer techniques have been used to define regions of homogeneity. Monophasic regions occur for  $0 \leq x \leq 0.01$  (where the structure is that of the 2H- $NbSe_2$  polytype),  $0.11 \leq x \leq 0.20$  (structure 4Hb), and  $0.30 \leq x \leq 1.00$  (structure 1T). It is proposed that vanadium substitutes for niobium in trigonal-prismatic coordination in only the first of these regions; otherwise, the vanadium goes into octahedral coordination and produces the 4Hb polytype by enhancing octahedral coordination of the niobium. The variation of structural parameters with composition is described in terms of a pure size effect attendant on the vanadium-for-niobium substitution.

(3) Michel Bayard, "Electrical and Magnetic Properties of Vanadium-Substituted Niobium Diselenide", published in Journal de Physique, 37, Colloque C-4, 169(1976).

The electrical conductivity, static magnetic susceptibility, and Hall voltage have been measured from room temperature to liquid helium on a series of carefully characterized vanadium-substituted niobium diselenides ( $\text{Nb}_{1-x}\text{V}_x\text{Se}_2$ ,  $0 < x < 0.30$ ). Relatively large temperature-dependent Pauli paramagnetism and quadratic dependence of resistivity on temperature suggest a strongly correlated electron gas. Anomalies in the Hall voltage and resistivity are consistent with a charge-density-wave transition. The effect of vanadium substitution is mainly to change the nature of the coordination and, thereby, the component layers of the polytype structure. The superconducting critical temperature was observed to drop strongly in the 2H phase and then flatten out as progressive vanadium substitution is accommodated in layers with octahedral coordination.

(4) Michel Bayard, "Anomalous Electrical and Magnetic Properties of Vanadium Diselenide", published in J. Solid State Chem. 19 325(1976).

Powder samples of  $\text{VSe}_2$  have been made by direct synthesis from the elements. Single-crystal specimens have been made by vapor phase transport in the presence of iodine. X-ray characterization indicated only the 1T polytype. Behavior was metallic over the range 1.5 to 300°K, but there were discontinuities at about 100°K in resistivity, magnetic susceptibility, and Hall voltage. These are apparently due to the onset of charge density waves. Below 50°K, there was a clear quadratic dependence of resistivity on temperature which combined with relatively high Pauli paramagnetism to indicate Baber-type

electron-electron scattering. No superconductivity was observed down to 1.5°K.

(5) Lynn Schneemeyer (cooperative effort with Rolfe Herber at Rutgers), "Lattice dynamics in covalent solids: Sn in  $\text{SnS}_{2-x}\text{Se}_x$  ( $0 \leq x \leq 2$ )", published in J. Chem. Phys. 68 3705(1978).

Mössbauer effect studies using the 23.8 keV gamma transition in  $^{119}\text{Sn}$  have been carried out on the system  $\text{SnS}_{2-x}\text{Se}_x$  ( $0 \leq x \leq 2$ ) on both microcrystalline powders and single crystal samples. The composition dependence of the isomer shift parameter for the single line resonance spectrum shows that the covalency increases as  $x$  increases; the 5s population of tin in  $\text{SnSe}_2$  is  $\sim 0.13$  greater than it is in  $\text{SnS}_2$ . From the temperature dependence of the area under the resonance curve it is possible to extract a Mössbauer lattice temperature  $\theta_M$  which is only weakly dependent on composition for samples prepared in an identical manner. Single-crystal orientation experiments with  $\text{SnS}_2$  and  $\text{SnSe}_2$  have been carried out at  $295 \pm 1^\circ \text{K}$  to investigate the anisotropy in the metal atom motion parallel and perpendicular to the crystallographic  $c$  axis (perpendicular and parallel to the easy cleavage plane). The vibrational anisotropy ratio,  $\langle x_{11} \rangle / \langle x_{\perp} \rangle$ , is found to be 2.25 in  $\text{SnS}_2$  and 1.58 in  $\text{SnSe}_2$  at room temperature. The absolute values of the tin atom vibrational amplitudes have been calculated using the recoil-free fraction data for metallic ( $\beta$ ) tin under identical conditions.

(6) Wayne Fisher, "Stoichiometry, Structure, and Physical Properties of Niobium Sulfide", to be published, manuscript in preparation.

A series of carefully characterized samples of niobium sulfide with stoichiometries near  $\text{NbS}_2$  have been prepared and studied in comparison with



other layered transition metal dichalcogenides. The goals were to determine the conditions under which samples of niobium sulfide with known stoichiometry and structure could be prepared, to determine how stoichiometry and structure affect the superconducting transition of these materials, and to examine the system for signs of a charge density wave. In the course of investigating this last problem, vanadium-doped niobium samples were made and their properties studied.

Samples of niobium sulfide were prepared from the elements by reaction at high temperature (generally  $950^{\circ}\text{C}$ ) followed by quenching from some annealing temperature (usually  $750^{\circ}\text{C}$ ). The stoichiometry of the product depended on the pressure of excess sulfur present, and the structure of the product depended on the stoichiometry. When  $x$  in  $\text{Nb}_{1+x}\text{S}_2$  was between 0.18 and zero, two phases were observed. The stoichiometric disulfide was the 2H polytype, and all the evidence from this study indicates that it is a line phase. Powder x-ray patterns exhibited some diffuse lines indicative of disorder. For  $0.07 < x < 0.18$ , 3R- $\text{Nb}_{1+x}\text{S}_2$  was obtained. The powder x-ray lines were sharp, indicative of good crystallinity. No evidence was obtained for the existence of a stoichiometric 3R polytype, nor was there any evidence for long range ordering of the interlayer niobium atoms in the nonstoichiometric material.

The nonstoichiometric 3R- $\text{Nb}_{1+x}\text{S}_2$  did not superconduct above  $1.5^{\circ}\text{K}$ . The stoichiometric polytype 2H- $\text{NbS}_2$  superconducted at about  $6.3^{\circ}\text{K}$  with a typical transition width of 200mK.

The nonstoichiometric 3R polytype had a temperature-independent,

Pauli-type, paramagnetic susceptibility with a slight, non-Curie-Weiss like temperature dependence. The susceptibilities provided no evidence for the existence of a charge density wave state in either the 2H or 3R polytype. Since the 2H polytype was a line phase, the CDW was not destroyed by nonstoichiometry. Also, there is no pressure dependence to its superconducting transition temperature, so it must have no CDW.

With respect to CDW, the 3R polytype exhibits more complicated behavior. A correlation noted by Thompson [Phys. Rev. Lett. 34 520(1975)] predicts the appearance of CDW for certain stoichiometries in this polytype. However, a 3R-to-2H structure change is observed at  $x = 0.07$  just where the  $c/a$  ratio would suggest a CDW is expected to appear. For those stoichiometries where a CDW was expected in the 3R polytype, the 2H stacking was preferred. An explanation for the stacking change may involve Coulomb interactions between incipient charge density waves in adjacent layers of the two polytypes. In the 3R polytypes, the layer-to-layer metal atom registries would require some of the CDW maxima to be close together in adjacent layers, but in the 2H polytype they would be well separated.

To test the hypothesis that it is an incipient CDW which drives the phase change, vanadium-doped materials were prepared. The random potential in the cation sublattice produced when a V atom substitutes for an Nb atom was expected to suppress any incipient CDW, and thereby suppress the 3R-to-2H phase change. All the vanadium-doped materials were the 2H polytype instead of the 3R expected.

The vanadium-doped materials showed interesting physical properties. They remained superconductors. The first 1.1% V dropped the  $T_c$  by one degree

to about  $5.3^\circ\text{K}$ , then  $T_C$  was nearly constant to  $4.4\%V$ . This behavior was in spite of the presence of a local moment on the V consistent with a  $d^1$  system.

The evidence suggests that a small amount of V substitutes for Nb on Nb sites in the layer, while the rest goes between the layers, driving the material farther and farther from a one-metal-to-two-sulfur stoichiometry as the vanadium content increases. The V in the layers causes the initial drop in superconducting transition temperature; that between the layers must have no effect on it, in spite of the local moment. Thus, the layers appear to act independently of what is between them.

(7) Lynn Schneemeyer, "Effect of Niobium Substitution on CDW anomalies in Vanadium Diselenide", J. Less-Common Metals, 62 343(1978).

Precise measurements of the static magnetic susceptibility have been made by the Faraday method over a range of temperature from  $1.3$  to  $300^\circ\text{K}$  on a series of niobium-substituted vanadium diselenides. The kink anomaly associated with onset of the CDW at  $117^\circ\text{K}$  in  $VSe_2$  is observed to move to higher temperatures as the niobium concentration is increased. In addition, plateaus appear in the susceptibility vs. temperature curve below the onset temperature. It is suggested that the plateaus are due to stepwise destruction of the Fermi surface. Transition to the commensurate state is observed at  $\sim 75^\circ\text{K}$  in pure  $VSe_2$ ; it is relatively insensitive to the doping level and is observed as an anomaly in the magnetic susceptibility even at a 10% doping level.

(8) Lynn Schneemeyer, "Effect of Nonstoichiometry on CDW in  $VSe_2$ ", to be published, manuscript in preparation.

A systematic investigation has been made of the effect of nonstoichiometry on the CDW state in vanadium diselenide. The effects were monitored by static

magnetic susceptibility measurements over the range 4.2-300°K. For the series  $V_{1+x}Se_2$  ( $0 < x < 0.12$ ) the onset temperature of the CDW kink anomaly was observed to decrease slightly and the magnitude of the susceptibility drop to decrease rapidly with increasing deviation from ideal stoichiometry. The behavior of the characteristic Curie tail of the liquid helium region, which became more pronounced with increasing nonstoichiometry, suggests that the excess vanadium, believed to be accommodated in interlayer sites, is primarily  $V^{3+}$ . Donation of electrons to the layer may act to reduce the strong trigonal distortion of the octahedral sites in  $VSe_2$  and thus broaden the  $d$  band. Such band filling may result in moving the Fermi Surface off a peak in the density of states and make CDW effects increasingly unfavorable.

(9) Lynn Schneemeyer, "Mixed Anion Molybdenum Dichalcogenides", to be published.

A series of samples  $MoS_{2-x}Se_x$  ( $0 < x < 2$ ) was prepared by direct reaction of the pure elements at 900°C. Powder x-ray patterns with copper  $K\alpha$  radiation showed a continuous series of solid solutions, all of the 2H polytype. The  $a$  parameter shows a nearly linear increase with increasing  $x$ , the  $c$  parameter follows a parabolic curve.  $c/a$  shows a maximum at  $MoS_{0.7}Se_{1.3}$ , which corresponds to the same anion ratio found for the maximum in the tungsten system. The nonlinear behavior of  $c$  vs.  $x$ , in violation of Vegard's law, appears to be due to protrusion of the much larger selenium atom into the van der Waals gap, causing a disproportionate increase in  $c$ .

(10) David Hodul, "The Chemistry of Metal-Nonmetal Transitions in Hafnium Dichalcogenides", to be published, manuscript in preparation.



There are two possible ways of producing a metal-nonmetal transition in hafnium dichalcogenides. Electrons can be added to the empty conduction band of semiconducting  $\text{HfS}_2$  or  $\text{HfSe}_2$  by group V doping, halide substitution for the chalcogen, or alkali metal intercalation. Alternatively, solid solutions can be made of a metal and an insulator, e.g.  $\text{TiS}_2$  and  $\text{HfS}_2$ ,  $\text{HfTe}_2$  and  $\text{HfSe}_2$ . Several of these avenues were investigated in an attempt to study a metal-nonmetal transition in these materials.

The materials  $\text{HfTe}_{2-x}$  ( $0 < x < 0.6$ ) and  $\text{HfS}_{2-x}$  ( $0 < x < 1$ ) were prepared and characterized, using powder x-ray and standard analysis techniques, to understand better the properties of the end members of the systems, i.e.  $\text{HfTe}_2$  and  $\text{HfS}_2$ . Optimal reaction conditions were determined and synthetic preparation of single crystals of  $\text{HfTe}_{2-x}$  was found possible. Homogeneous products could not be made in the systems  $\text{Hf}_{1-x}\text{Te}_{2-x}$  ( $0 < x < 1$ ) or  $\text{Hf}_{1-x}\text{S}_{2-x}$  ( $0 < x < 1$ ), as the dichalcogenide is always formed.

The system  $\text{HfSe}_{2-x}\text{Te}_x$  is homogeneous with the 1T structure over the whole range  $0 < x < 2$ . It shows a metal-nonmetal transition at  $x = 0.1$ , as determined by magnetic susceptibility and electrical conductivity studies. Nonlinear variation of the  $c/a$  ratio as a function of composition in these hexagonal materials is explained by a model using hard-sphere packing and changes in ionicity.

The materials  $\text{Nb}_x\text{Hf}_{1-x}\text{S}_2$ ,  $\text{Mo}_x\text{Hf}_{1-x}\text{S}_2$ ,  $\text{Li}_x\text{HfS}_2$ ,  $\text{Ti}_x\text{HfS}_2$ , and  $\text{V}_x\text{HfS}_2$  were prepared by various synthetic methods, and characterized by powder x-ray techniques.  $\text{Li}_x\text{HfS}_2$  showed an ESR signal, but none of these compounds was found to be superconducting above 1.5° K.

(11) Alex Chang, Philippe Molinié, "Electric and Magnetic Properties of Vanadium-Substituted Titanium Disulfide", Journal de Physique, 39 (C6), 1070(1978).

The electrical conductivity, static magnetic susceptibility, and Hall voltage have been measured from room temperature to liquid helium on a series of vanadium-substituted titanium disulfides,  $V_xTi_{1-x}S_2$  ( $0 < x < 0.10$ ).  $T^2$  dependence of resistivity was observed in dilute crystals ( $0 < x < 0.02$ ) with resistivity minima at  $\sim 20^\circ K$  suggesting existence of a local moment in agreement with magnetic susceptibility measurements. Crystals with higher vanadium concentration ( $0.04 < x < 0.10$ ) exhibit semiconducting behavior with a temperature-dependent "band gap." We suggest for this range Anderson localization of conduction electrons due to potential fluctuation created by randomly distributed vanadium atoms. This localization is complicated by magnetic ordering at low temperature. Magnetic susceptibility data show Curie-type behavior corresponding to  $V^{3+}(d^2)$  with ferrimagnetic ordering at low temperature. Anomalies in resistivity were observed at temperatures corresponding to ordering in the susceptibility.

(12) Alexander Chang, "Synthesis and Characterization of Vanadium-Substituted Titanium Disulfide", to be published, manuscript in preparation.

Single crystals of  $V_xTi_{1-x}S_2$  ( $0 \leq x \leq 0.5$ ) were prepared by vapor transport reaction. The crystals were characterized by X rays for single phase composition, ion microprobe analysis for homogeneity, semiquantitative optical emission spectrography for impurity, and neutron activation and colorimetry for vanadium content.

A.C. resistivity and Hall voltage were measured on single crystals using standard van der Pauw and 5-probe misalignment resistor techniques,

respectively, from ambient temperature down to 1.9° K. Static magnetic susceptibility was measured using a Faraday balance over the same temperature range. Raman scattering experiments were performed in an attempt to explain some observed resistivity anomalies.

For dilute samples,  $x < 0.021$ , resistivity minima observed were explained in terms of a Kondo effect. The relationship  $T_{\min} \sim c^{\frac{1}{2}}$  was observed, where  $c$  is the concentration of magnetic impurity. For  $x = 0.021$ ,  $\rho \sim \log T$  was observed for  $T < T_{\min}$ . For  $T > 40^\circ \text{K}$ , observed  $T^2$  dependence of resistivity was investigated by comparison with two existing models: electron-hole scattering of "semimetallic  $\text{TiS}_2$ " by Thompson, Kukkonen, and Maldague and the Fivaz mechanism proposed by Wilson.

More heavily doped samples  $0.039 \leq x \leq 0.078$  exhibit thermally activated conductivity. Resistivity behavior of these crystals was explained using the Anderson localization model and compared with other Anderson localized systems.

Whereas  $\text{TiS}_2$  shows only temperature-independent paramagnetism, vanadium-doped samples show a composition- and temperature-dependent magnetic moment. Such a moment is believed to arise from interlayer vanadium, possibly as  $\text{V}^{3+}$ , as observed in  $\text{V}_5\text{S}_8$  and  $\text{V}_5\text{Se}_8$ . Magnetic effects play an essential role, especially at low temperature, in causing anomalous resistivity behavior.

(13) Rob Hemmel, "X-Ray Diffraction Studies and Magnetic Measurements of the  $\text{VSe}_{2-x}\text{S}_x$  System."

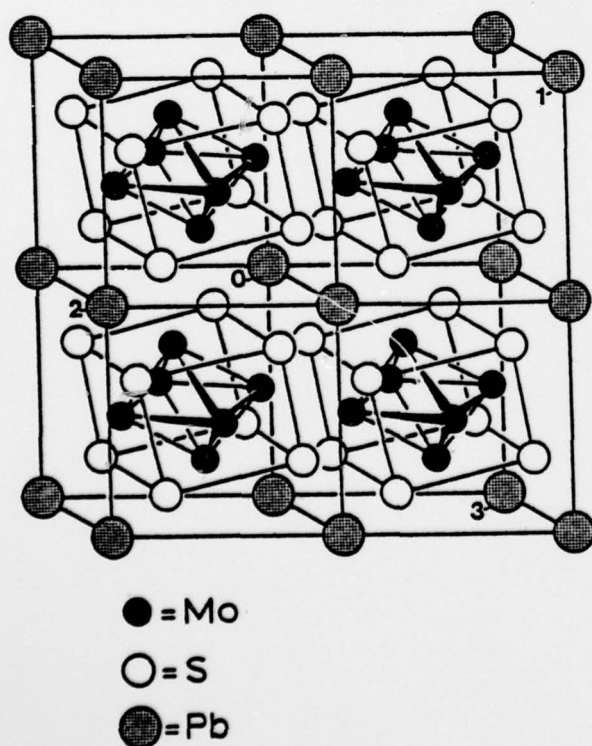
The series of mixed-anion compounds  $\text{VSe}_{2-x}\text{S}_x$  ( $0 < x < 0.20$ )

has been prepared by reaction of the elements at 800° C. X-ray diffraction studies indicate that  $a$  decreases linearly with  $x$  but  $c$  shows a parabolic drop-off. Magnetic susceptibility measurements over the range 4.2-300° K show a slight decrease in the CDW kink anomaly temperature from 114° K for  $x = 0.01$  to 106° K for  $x = 0.10$ .

#### (D) CHEVREL PHASES

(1) Frank Delk, "Correlations between Structure and the Superconducting Transition Temperature in Chevrel Phase Molybdenum Chalcogenides", to be published in Solid State Communications.

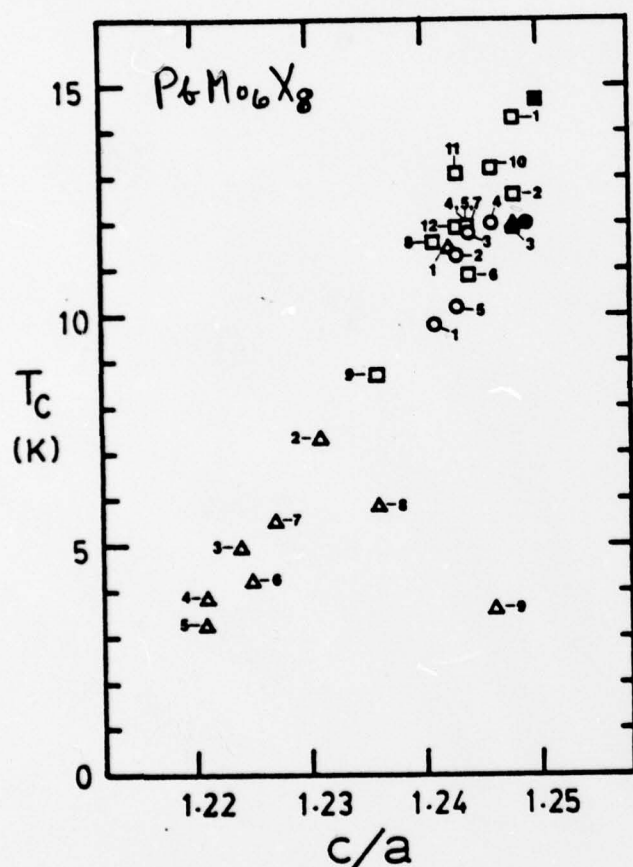
The class of molybdenum chalcogenides  $M Mo_6 X_8$  (where  $M = Pb, Sn, \text{Rare Earth, or vacancy and } X = S, Se, \text{ or } Te$ ), are known as Chevrel phases. One of their most intriguing aspects is their wide variability of superconducting transition temperature and lack of obvious correlations with ternary element or structure.

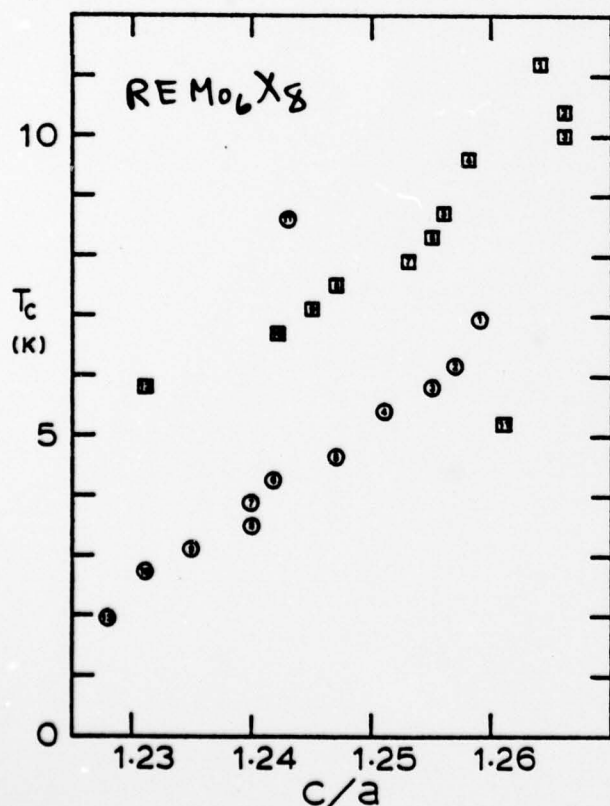
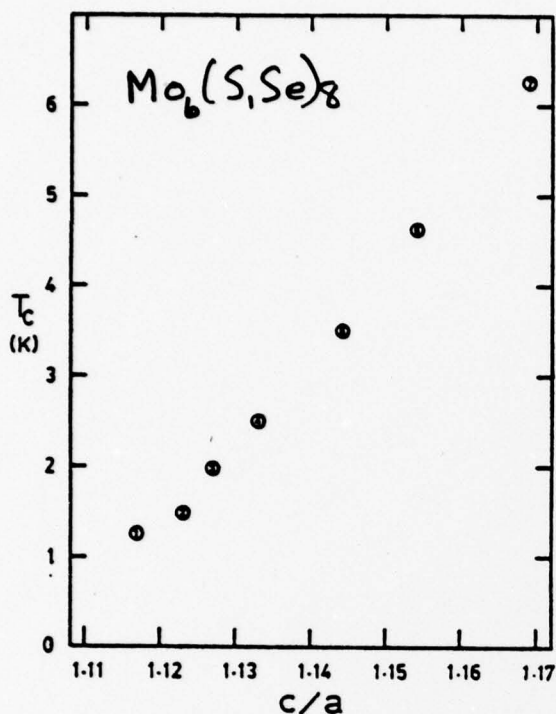


Most of these materials crystallize in the rhombohedral space group  $R\bar{3}$ . The characteristic feature of the lattice is the  $Mo_6 X_8$  unit. The anions  $X$  form a distorted cube with the Mo atoms occupying face center positions and forming a  $Mo_6$  octahedron. When a large ternary element is present, (e.g., Pb, Sn, Rare Earth, . . .) it occupies positions on a nearly cubic lattice, since the rhombohedral angle is nearly 90° in these materials.



The  $\text{Mo}_6\text{X}_8$  units occupy the cubes formed by the ternary element, sharing a common three-fold axis with the ternary element lattice. The principal distortion from cubic is a rotation of  $\sim 25^\circ$  of the  $\text{Mo}_6\text{X}_8$  about the axis with respect to the other lattice, this being the  $\bar{3}$  axis. The hexagonal  $\underline{c}$  unit vector is the vector along  $\bar{3}$  between two ternary atoms. The  $\underline{a}$  unit vectors are perpendicular to the  $\underline{c}$  axis.





Similarly if  $T_c$  is plotted as a function of  $c/a$  for  $\text{Mo}_6(\text{Se},\text{S})_8$ , the result is again a linear dependence of  $T_c$  on  $c/a$ .

For the rare earth ternary superconductors, it has been suggested [Bull. Am. Phys. Soc. 23 347(1978)] that  $T_c$  is depressed by pair breaking due to a weak exchange interaction between the  $d$  conduction electrons and the rare earth ions. If corrections are applied for this effect, the corrected transition temperatures again show a strong linear correlation between  $T_c$  and  $c/a$  ratio. The  $\text{YbMo}_6\text{X}_8$  materials are anomalous but are believed to contain  $\text{Yb}^{2+}$  unlike the typical rare earth  $\text{RE}^{3+}$ .

It is apparent that  $T_c$  is a very sensitive function of the  $c/a$  ratio. The  $c$  parameter gives a direct measure of the strength of the interaction along the  $\bar{3}$  axis. The interaction likewise depends on the size of the chalcogen on

the  $\bar{3}$  axis and the size of the ternary element and its delocalization from the  $\bar{3}$  axis. It is believed to be quite weak as is evidenced by the existence of superconductivity in the rare earth ternaries, soft phonon modes associated with the ternary element, and suspected coexistence of magnetic ordering and superconductivity.

The  $\underline{a}$  parameter is related to intercluster interaction. It reflects increasing chalcogen size by increasing. A more subtle effect is expected to result from varying charge transfer to the Mo  $\underline{d}$  conduction band. Yvon and Paoli [Solid State Comm. 24 41(1977)] showed that the Mo-Mo intracluster distance decreased with increasing charge transfer to the conduction band, showing its bonding nature. Inasmuch as the intercluster interaction is bonding, an increase in the charge transfer should be accompanied by a decrease in the  $\underline{a}$  parameter. Indeed, this is seen to be the case.  $\text{YbMo}_6\text{S}_8$  and  $\text{EuMo}_6\text{S}_8$  exhibit anomalously large  $\underline{a}$  parameters relative to the other rare earth molybdenum sulfides. This is due to the smaller charge transfer since these materials are thought to contain  $\text{Yb}^{2+}$  and  $\text{Eu}^{2+}$  ions instead of  $\text{RE}^{3+}$  as found in the other rare earth ternaries.

The  $c/a$  ratio is then a measure of the bonding along the  $\bar{3}$  axis normalized for chalcogen size and electronic changes. Increase in this ratio indicates a weakening of the interactions and decreases, a strengthening. The strong dependence of  $T_c$  on  $c/a$  is consistent with the strong negative dependence of  $T_c$  on pressure observed by Shelton. Increased pressure would preferentially collapse the soft axis  $\underline{c}$  reducing  $T_c$ .

It is easy to see that the frequency of the longitudinal phonon mode

will be directly related to the strength of the interaction and hence to  $c/a$ . The expectation is that as  $c/a$  increases, the frequency will decrease. The importance of longitudinal modes to superconductivity in these materials has been discussed before. Bader et al. measured the phonon spectra of  $\text{PbMo}_6\text{S}_8$  and  $\text{SnMo}_6\text{S}_8$  and concluded the soft modes associated with libration of the  $\text{Mo}_6\text{X}_8$  unit were important for superconductivity. More recently Culleto and Pobell studied the isotope effect on the superconducting transition temperature and concluded that it is either the soft longitudinal modes or the hard internal modes of the  $\text{Mo}_6\text{X}_8$  units which are important for  $T_c$ .

The strong dependence on the  $c/a$  ratio that  $T_c$  exhibits is consistent with the longitudinal modes contributing to the superconductivity in these materials. The puzzling aspect is the apparent inverse dependence of  $T_c$  on the phonon frequency. This is in apparent contradiction to the isotope effect and the dependence predicted in the BCS theory. A possible explanation is that increasing the  $c/a$  ratio produces better electron-phonon coupling and this effect dominates. Culleto and Pobell report the lattice parameters of the isotopically substituted  $\text{Mo}_6\text{Se}_8$  series are practically identical. Hence they observe the pure isotope effect.

The anomalous points  $\text{PbMo}_6\text{Se}_8$ ,  $\text{YbMo}_6\text{S}_8$ , and  $\text{YbMo}_6\text{Se}_8$  can all be understood in terms of the differing charge transfer to the Mo  $d$  conduction band, with respect to the relevant series. Both of the ytterbium Chevrel phases are believed to contain mostly  $\text{Yb}^{2+}$  and therefore transfer  $\sim 1$  less electron to the conduction band than the other rare earth ternaries. It has been suggested that in the Chevrel phase selenides, the selenium ions



have a formal charge less than -2 and hence there is an increased charge transfer to the conduction band with respect to the sulfides. [J. Solid State Chem. 22 87(1977)] . Anderson et al. have placed the Fermi level in  $\text{PbMo}_6\text{S}_8$  at a peak in the density of states. Thus,  $\text{YbMo}_6\text{S}_8$  is expected to fall on the curve generated by the lead ternaries based on its similar charge transfer. This is seen to be the case. As the charge transfer increases and the conduction band fills, there will be a sharp drop in the density of states. This would lead to a concomitant drop in the transition temperatures seen in a group with similar filling of the conduction band. As the charge transfer continues to increase, a minimum in the density of states will be reached and a further increase will be accompanied by an increase in the density of states. This will outwardly manifest itself in higher transition temperatures in a series of materials. This is precisely what is observed as the charge transfer is increased from the Pb and Yb Chevrel phase sulfides to the Pb and Yb Chevrel phase selenides, to the rare earth Chevrel sulfides, and finally to the rare earth Chevrel selenides. This is consistent with placing the Fermi level at the lower peak in the density of states of the Eg conduction band.

It is clear that the superconducting transition temperature is a sensitive function of the crystallographic  $c/a$  ratio, charge transfer remaining constant. As noted, this is consistent with the longitudinal phonon mode's being important for superconductivity. However, the inverse dependence of  $T_C$  on frequency, opposite that expected, leads us to suggest that the electron-phonon coupling is strongly dependent upon  $c/a$  and dominates the observed  $T_C$ . Since changes in stoichiometry can widely vary  $c/a$ , the wide range of  $T_C$ 's

reported in the literature is more easily understood.

### III. UNFINISHED WORK

The Chevrel phases remain a tantalizing enigma. All the evidence indicates that standard preparations result in multiphase products. We have tried to grow single crystals (flux growth, vapor phase transport, minimum-gradient mineralization) with a singular lack of success. The precise stoichiometry of the superconducting phase, particularly for the rare earth Chevrel compounds, is not established. We have reason to believe that sulfur deficiency is critical in fixing the structure,  $c/a$ , and  $T_c$ . Because the Chevrel phases have high critical temperatures and high critical fields and because the copper analogue has apparently been successfully fabricated into a magnet coil, it would be worthwhile to investigate the stoichiometry problem in greater depth so as to have a basis for optimizing parameters.

We have also not been able to complete our project of investigating the mixed-anion series  $\text{YbMo}_6(\text{S},\text{Se})_8$ . These materials should be characterized by a systematic decrease in the density of states, and their study would be useful in separating the contributing parameters. Most informative would be combined divalent and trivalent doping to separate out size and electron density effects.

With respect to the hexaborides, an important study left unfinished is the insertion of beryllium as a substitutional replacement for part of the boron in the covalent-frame boron network. This should have the effect of introducing electron holes in the  $B_6$  band and reduce the electron pressure so that the incipient tendency of  $\text{La}^{3+}$  to go  $\text{La}^{2+}$  could be minimized. It is believed that if the formation of trace  $\text{La}^{2+}$  could be avoided, the potentially

high critical temperature of  $\text{LaB}_6$  might be attained.

#### IV. PERSONNEL

The people who contributed to this project are:

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Principal Investigator

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Dr. Johannes K. Petersen (8/1/75-7/31/76)  
Dr. Rob Hemmel (4/26/78-12/31/78)

Postdoctoral Research  
Associates supported  
by AFOSR

Dr. Rudolf Sobczak (7/27/76-7/26/77)  
Dr. Bernard Mentzen (7/15/74-7/14/75)  
Dr. Philippe Molinie (8/24/77-8/23/78)

Postdoctoral Research  
Associates supported by  
Materials Science Center  
at Cornell University

Dr. Benoy Chakraverty (5/10/77-1/30/78)  
Dr. Andrejs Lusis (9/2/76-5/15/77)

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Associates

Roger Williams

Undergraduate Technician

Linda Weise  
Christina Fulman  
Sharon Brautigam

Secretarial

## V. PUBLICATIONS

(a) Four Ph.D. thesis were awarded during the period of this project:

Alexander T. Chang, "Electric and Magnetic Properties of Vanadium-Substituted Titanium Disulfide."

Wayne G. Fisher, "Stoichiometry, Structure, and Physical Properties of Niobium Sulfide."

David T. Hodul, "The Chemistry of the Metal-Nonmetal Transitions in Hafnium Dichalcogenides."

Lynn F. Schneemeyer, "The Effect of Niobium Substitution and of Nonstoichiometry on the Charge Density Wave Transition in Vanadium Diselenide."

(b) The following papers under this sponsorship have been published or are in press:

"Concentration Dependence of Superconductivity in Rubidium Tungsten Bronzes," David R. Wanlass and M.J. Sienko, J. Solid State Chem. 12 362-369(1975).

"Low-Temperature Magnetic Susceptibility of Uranium and Rare Earth Tungsten Oxide Bronzes," Jack F. Thomas and M.J. Sienko, J. Chem. Phys. 61 3920-3924(1974).

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(c) The following manuscripts are in various stages of preparation for submission to the journals:

"Crystal Data for Mixed-Anion Molybdenum Dichalcogenides,"  
Lynn F. Schneemeyer and M.J. Sienko.

"Synthesis and Characterization of Vanadium-Substituted Titanium Disulfide," Alex T. Chang and M.J. Sienko.

"Effect of Nonstoichiometry on the Charge Density Wave Transition in Vanadium Diselenide," Lynn F. Schneemeyer and M.J. Sienko.

"The Chemistry of Metal-Nonmetal Transitions in Hafnium Dichalcogenides," David T. Hodul and M.J. Sienko.

"Stoichiometry, Structure, and Physical Properties of Niobium Sulfide," Wayne G. Fisher and M.J. Sienko.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) <p>→ The objective of this research was to study the effect of chemical composition on superconductivity in chemical compounds. Four kinds of compounds were investigated: tunnel-structure tungsten bronzes, covalent-frame hexaborides, layered-structure transition metal dichalcogenides, and Chevrel-type molybdenum ternaries. In the tungsten bronzes, it was found that changing electron density was less important than enhancing electron-phonon coupling, by approach to a crystallographic structure change boundary. In the metal →</p>										

Block 20 (ABSTRACT), continued:

hexaborides, it was shown that lattice expansion was less effective than decreasing conduction electron density in depressing the superconducting critical temperature, but even more effective was presence of magnetic ions in the metal sublattice. This was found to be the most likely reason for the very low critical temperature of lanthanum hexaboride. In the layered dichalcogenides, insertion of magnetic ions between the layers was found to be less effective in depressing critical temperature than either substitution of magnetic ions within the layers or departure from stoichiometry. The latter was found to lead to a change in polytype which could be correlated with the onset temperature of a charge density wave. In the Chevrel-type compounds, a new correlation was found between superconducting critical temperature,  $c/a$  lattice parameter ratio, and deviation from stoichiometry.